

Phase Formation and Stability: Composition and Sample-Size Effects

A Final Report of the Research Performed Under NASA Grant NCC 8-049

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Task Objectives

Kinetic studies of phase transformations are important for obtaining estimates of parameters, such as the nucleation rate and the growth velocity, that are key to controlling phase microstructures. Differential scanning calorimetry (DSC) and differential thermal analysis (DTA) are attractive experimental techniques for studies of phase transformations since they are easily made on small quantities of samples. Further, such experiments should be readily automated, making it possible to obtain data remotely, such as in a microgravity environment. Under a previous NASA grant (NAG 8-873), we developed realistic computer simulations of first-order phase transformations, resulting in improved methods for the analysis of kinetic studies of isothermal and nonisothermal phase transformations. These new methods allowed kinetic parameters for nucleation and growth to be determined from peak profile studies of DSC and DTA data.

Those studies were limited to polymorphic transformations, where the compositions of the initial and final phases were identical. It is desirable to extend the ideas developed there to the more common case of phase transformations involving solute partitioning during nucleation and growth. One major objective under NASA grant NCC 8-049 was therefore to carry out limited studies of nucleation in partitioning systems to investigate, experimentally and theoretically, the effects of a changing composition on the time dependent nucleation rates. Measurements of the time-dependent nucleation rate were made as a function of $[\text{SiO}_2]$ in $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$ glasses. A second objective was to establish the feasibility of making undercooling measurements of Ti-based alloys made near quasicrystal forming compositions, using the NASA drop tube facility at Marshall Space Flight Center.

Task Description

Crystallization of $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$ glasses was studied by DTA and DSC. Direct measurements of the homogeneous nucleation rate as a function of $[\text{SiO}_2]$ were made following a two-step annealing treatment. Samples were first annealed for different amounts of time in a temperature range where the nucleation rate is known to be significant. All samples were

subsequently annealed for the same time at a higher temperature to grow the nuclei produced in the first anneal to an observable size. The number of nuclei generated are consequently determined directly as a function of annealing time at the nucleating temperature. The slope of these data is the time-dependent nucleation rate.

Changes in driving free energy as a function of composition were determined by measurements of the change in liquidus temperature, measured by DTA. Assuming the Turnbull approximation, then, $\Delta G = (\Delta H_f/T_m) (T - T_m)$. Changes in the diffusion coefficient with composition were estimated from measurements of the growth velocities obtained by optical and electron microscopy and from the measured induction times for nucleation. Existing computer programs that predict time-dependent nucleation behavior by modeling directly the evolution of the cluster distribution were used to consistently fit the steady state and time-dependent nucleation rates. Computer models developed under previous NASA grant NAG 8-873 were used to model DTA and DSC crystallization of these glasses, using the measured nucleation rates and growth velocities. The effects of finite particle size on the nonisothermal transformation kinetics were included for the first time, using an analytical expression developed under the support of this grant and the previous one.

Alloys for drop tube experiments were produced at Washington University by arc-melting in an inert gas atmosphere. They were sent to Huntsville to be dropped in the NASA 100 m drop tube at Marshall Space Flight Center. Samples were returned to our research group for microstructural and phase information, using scanning electron microscopy, transmission electron microscopy and x-ray diffraction.

Task Significance

Despite the popularity of DSC and DTA measurements, few methods for the quantitative analysis of such calorimetric data exist. This is particularly true for nonisothermal data, where most methods are based on erroneous assumptions that generally result in misinformation. Even for isothermal studies, however, proper account is generally not taken of the transformation microstructure, making most interpretations suspect. Further, though DSC/DTA data are often obtained from quantities of fine powder, finite particle size effects are ignored. This can seriously effect the analysis of calorimetric data taken from powders; it will have a profound effect on calorimetric signals from nano-sized particles.

Our computer models provide realistic descriptions of nucleation and growth under isothermal and nonisothermal conditions by simulating directly the evolution of the non-equilibrium cluster distribution underlying nucleation phenomena. Finite-size sample effects are included naturally. These techniques allow, for the first time, the quantitative analysis of DSC and DTA data. They also enable real-time experimental studies of phase stability and transformation in a microgravity environment.

Our previous success in describing polymorphic transformations suggests the potential of these same techniques for application to the more common case of phase transformations involving partitioning. Though diffusion-limited growth has been well studied, only limited

investigations of the effects of partitioning on the nucleation rate exist. The new information gained from the initial studies undertaken under this NASA grant (NCC 8-49) has directed the extension of the classical theory of nucleation and the calorimetric computer models to some nonpolymorphic transformations. Our studies also show that previous explanations of the change in crystal nucleation rates in $\text{Na}_2\text{O} \cdot 0.2\text{CaO} \cdot 0.3\text{SiO}_2$ glasses as a function of $[\text{SiO}_2]$ were incorrect.

Research Results

The first measurements of the time-dependent nucleation rates as a function of composition in any system were completed. These were fit to the evolving cluster distribution using a numerical model developed previously by us. The numerical model simulating DSC and DTA transformation kinetic studies, which was first developed by us under a previous NASA grant (NAG 8-873) was tested further, showing good agreement with experimental data. The extension of that model to include finite size effects was completed. The initial feasibility studies for processing Ti-based quasicrystal forming alloys in the Huntsville Drop Tube facility were completed successfully. Significant results from this research include:

1. First measurements of the time-dependent nucleation rates as a function of composition - Nucleation rates of the stoichiometric crystalline phase, $\text{Na}_2\text{O} \cdot 0.2\text{CaO} \cdot 0.3\text{SiO}_2$, from quenched glasses made with different $[\text{SiO}_2]$ were determined as a function of time for different temperatures and glass compositions. The nucleation rates decreased significantly with increasing SiO_2 . The crystal growth velocity and the induction time for nucleation showed a weak dependence on glass composition.
2. Role of Composition Dependent Interfacial Energy on Nucleation Kinetics - Large changes in nucleation rate with $[\text{SiO}_2]$ with only small corresponding changes in the growth velocity and the induction time indicate that atomic mobility changes with glass composition are not the origin of the composition dependent nucleation rate. This is in contradiction to an earlier suggestion made on the basis of steady state nucleation rates alone. Further, our measurements of the liquidus temperatures as a function of composition confirmed that changes in the driving free energy for crystallization cannot explain the results. That a monotonic decrease in the nucleation rate with increasing $[\text{SiO}_2]$ is observed, both below and above the stoichiometric composition, suggests that an increased importance for nucleation of a coupled diffusive flux in the glass with the interfacial attachment flux is not indicated. Only a change with composition of the interfacial energy between the crystal cluster and the glass can explain the experimental data. To our knowledge, this is the first example of this effect in any system.
3. Extension of Computer Model of Time-Dependent Nucleation - Numerical calculations for time-dependent nucleation made earlier by us for polymorphic transformations were extended to model these new data for a partitioning system. Changes in the driving free energy for crystallization with composition were estimated from the measured liquidus temperatures. Changes in the atomic mobility were estimated from growth velocity data. Using these parameters, both the measured steady-state nucleation rates and the induction times were fit

quantitatively by assuming a composition dependent interfacial energy (Fig. 1). This is the first occasion for the modeling of a composition dependent transient nucleation in any system.

4. Differential Thermal Analysis of Glass Crystallization as a Function of Composition - The nonisothermal crystallization of $\text{Na}_2\text{O} \cdot 0.2\text{CaO} \cdot 0.3\text{SiO}_2$ glasses were studied as a function of $[\text{SiO}_2]$ by differential thermal analysis. The peak temperatures and peak widths, increase with $[\text{SiO}_2]$, while the peak intensity decreases. This is consistent with the measured decrease in the nucleation rate with increasing $[\text{SiO}_2]$.
5. Extension of Computer Models of Isothermal and Nonisothermal Transformations - A realistic computer model of isothermal and nonisothermal phase transformation started under NASA grant NAG 8-873 was extended under NASA grant NCC 8-049 to include changes in the nucleation rate with composition due to changes in the interfacial free energy.
6. First Demonstration of the Effects of Time-Dependent Nucleation on Nonisothermal Crystallization Behavior - Experimental studies of the DSC transformation peak profiles for $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ glasses showed identical behavior, whether the glasses were held for a specific time at the peak nucleation rate temperature or were scanned through the nucleation rate at a rate corresponding to that time. This is an unexpected result, not consistent with a steady state nucleation rate. An application of our model of phase transformations confirmed that this result reflects a complicated time-dependent nucleation behavior during the nonisothermal scan. This is first demonstration of the importance of time-dependent nucleation for glass devitrification. It also demonstrates the power of our modeling approach for analyzing thermoanalytic data.
7. Demonstrated ability to levitate and melt Ti-3d transition metal -Si-O samples in the NASA 100 m Drop-Tube - Samples of Ti-Cr-Si, Ti-Cr-Si-O, Ti-Mn-Si-O and Ti-Zr-Ni, which form phases with local icosahedral order, were prepared at Washington University by arc-melting pure elements in an argon atmosphere. Alloy ingots were levitated and dropped in the NASA 100 m drop-tube, located at Marshall Space Flight Center, Huntsville. The sample size was optimized to improve position stability of the samples in the rf coils. Techniques were developed for preparing thin slices for TEM studies. Initial TEM and SEM studies of the microstructure were carried out. These studies fulfill the aim of this grant, to demonstrate the feasibility of making undercooling and subsequent microstructural studies of metal alloys made near quasicrystal forming compositions.

Summary of research results

The preliminary investigations proposed for this grant were successful. Our first studies of the composition dependence of the time-dependent nucleation rate in any system demonstrated the importance of changes in the interfacial free energy in the nucleation kinetics. A computer model developed previously by us to simulate isothermal and nonisothermal first order phase transformations has been further tested and extended to include a composition dependent nucleation rate. Previously we demonstrated the importance of time-dependent nucleation on

glass formation. Under this grant, the importance of time-dependent nucleation rates in devitrification was established. Further, our computer model was shown to describe accurately the complicated nucleation behavior resulting from the thermal history dependence of the cluster evolution.

Papers and presentations on work supported by this contract

Several papers related to this work have been written or have appeared in print during this funding period. Results were presented as invited and contributed conference presentations.

Publications (submitted, in press, or appearing in print during this grant period)

1. "Kinetic Analysis of Nonisothermal Crystallization," K. F. Kelton, Proceedings of the MRS, Thermodynamics and Kinetics of Phase Transformations (J. S. Im, B. Park, A. L. Greer and G. B. Stephenson, eds), **398** (1995).
2. "Effect of Pt Doping on Nucleation and Crystallization in $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ Glass: Experimental Measurements and Computer Modeling," K. Lakshmi Narayan, K. F. Kelton and C. S. Ray, *J. Non-Cryst. Solids*, **195** 148-157 (1996).
Most of the research in this paper was performed under previous NASA grant (NAG 8-873).
3. "Nonisothermal Calorimetric Studies of the Crystallization of Lithium Disilicate Glass," C. S. Ray, D. E. Day, W. Huang, K. Lakshmi Narayan, T. S. Cull and K. F. Kelton, *J. Non-Cryst. Solids*, **204**, 1 (1996).
4. "Computer Modeling of Nonisothermal Crystallization," K. F. Kelton, K. Lakshmi Narayan, L. E. Levine, T. C. Cull and C. S. Ray, *J. Non-Cryst. Solids*, **204**, 13 (1996).
5. "Finite size corrections for the Johnson-Mehl-Avrami-Kolmogorov Equation," L. E. Levine, K. L. Narayan and K. F. Kelton, *J. Mater. Res.* (1996 in press).
6. "Analysis of Crystallization Kinetics," K. F. Kelton, *Mat. Sci. and Eng.* (1996, in press).
7. "First Measurements of Time-Dependent Nucleation as a Function of Composition in $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$ Glasses," K. Lakshmi Narayan and K. F. Kelton, *J. Non-Cryst. Solids* (Dec. 1996, submitted).

Invited Seminars

1. "Kinetic Analysis of Nonisothermal Crystallization," K. F. Kelton, Invited Presentation. Materials Research Society, Boston, MA, November 1995.
2. "From Liquids to Crystals," Distinguished Speaker Series, Arkansas Tech University, Russellville, AR, 19 April, 1996.

3. "Analysis of Crystallization Kinetics," Invited Presentation, Proceedings of the Ninth International Conference on Rapidly Quenched Metals, Bratislava, Slovakia, August, 1996.
4. "Nucleation," K. F. Kelton, Invited Presentation, Phasenubergange in Metallen, Institut für Raumsimulation, DLR, Cologne, Germany, 4-5 June, 1996.

Conference Presentations

1. "Composition Effects of Nucleation and Growth in $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$ Glasses," K. Lakshmi Narayan and K. F. Kelton, Mid-Western Solid State Conference, 13-14 October 1995, St. Louis, MO.
2. "Crystallization Behavior in $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$ Glasses." K. Lakshmi Narayan and K. F. Kelton, American Physical Society Meeting, 18-22 March, 1996, St. Louis, MO.
3. "Composition Dependence of the Time-Dependent Nucleation Rate in $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$ Glasses," American Physical Society Meeting, 17-21 March 1997, Kansas City, KS.
4. "Phase Formation and Stability: Composition and Sample-Size Effects," K. F. Kelton, Microgravity Materials Science Conference, Huntsville, AL, 10-11 June, 1996.

Future Work

Building on the successes of the past two grants, we are investigating more deeply composition effects on nucleation and growth under NASA grant NAG 8-898. In particular, research carried out under NCC 8-049 was designed to determine the feasibility for deeper investigation of the composition dependence of nucleation behavior. The success of that work has led to the following investigations that are already underway:

1. Nucleation studies in $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$ glasses prepared with different $[\text{SiO}_2]$ as a function of pre-annealing treatments. We have demonstrated previously that preannealing treatments at specific times and temperatures can cause the nucleation rate to go through a maximum with time. The location and intensity of these maxima are dependent on the annealing conditions and provide a more detailed investigation of the cluster evolution underlying time-dependent nucleation. These studies will allow the conclusions drawn in research funded by NCC 8-049, that the composition dependence of the nucleation rate in the system studied is due to a changing interfacial energy, to be tested more rigorously.
2. Measurements of the time-dependent nucleation rates and growth velocities in select silicate and metallic glasses. In particular, the recently discovered metallic glasses that are highly resistant to crystallization are under investigation, potentially allowing the first quantitative measurements of nucleation rates in a metallic glass.
3. Determination of liquidus temperatures and growth velocity for glasses as a function of composition. DSC and DTA will be used to determine the liquidus temperatures in silicate

and metallic systems to estimate changes in the driving free energy for crystallization. Growth velocities will be estimated by microscopic investigations of annealed samples to estimate changes in the kinetics.

4. Undercooling measurements of liquids that form quasicrystals and related tetrahedrally close-packed crystalline structures as a function of composition. Undercooling measurement are underway in collaboration with M. Robinson, using the NASA 100 m drop-tube located at Marshall Space Flight Center. Levitation measurements of undercooling are being made in collaboration with D. Herlach, DLR, Cologne, Germany. A collaborative measurement between my group and Herlach's group, using the TEMPUS facility, will be made on a shuttle flight in March, 1996.
5. Extension of the numerical model to include both kinetic and thermodynamic effects on the time-dependent nucleation behavior. The computer model for nucleation and growth is being extended to take full account of partitioning effects. Guided by the data collected from NCC 8-049 and the current grant, the classical theory of nucleation is being modified to take account of the coupled fluxes of diffusion in the original phase and interfacial attachment.

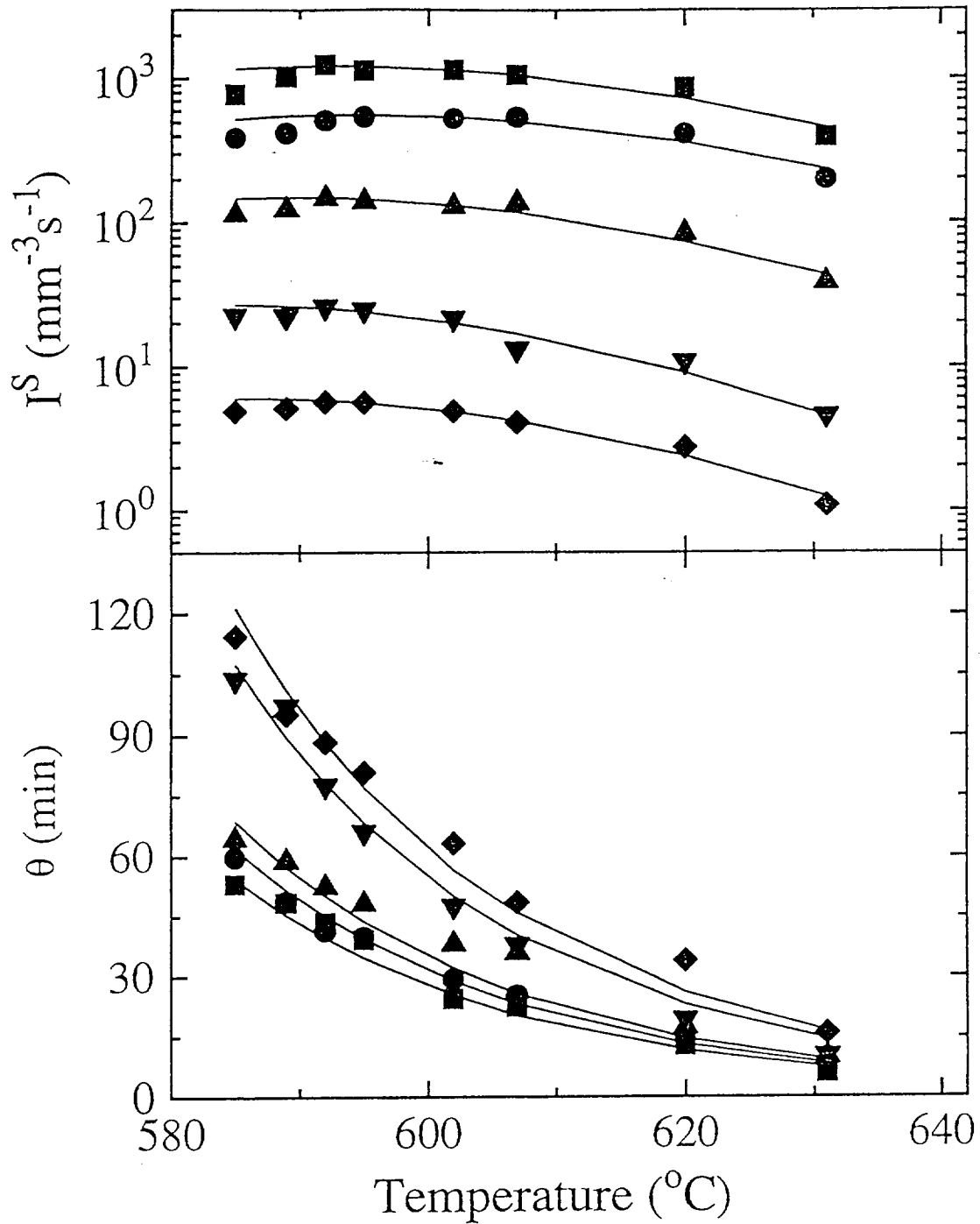


Fig. 1 Crystal steady state nucleation rates (a) and induction times (b) as a function of temperature for glasses of different composition: ■ - [SiO₂] = 0.494; ● - [SiO₂] = 0.5 ▲ - [SiO₂] = 0.506; ▼ - [SiO₂] = 0.52; ◆ - [SiO₂] = 0.53. The direction of increasing [SiO₂] is indicated by the arrows. Uncertainties in (a) are comparable to the symbol sizes. The solid lines through the points are a fit to the steady-state nucleation rates assuming a composition-dependent interfacial energy (computed data are given in Table 1).

Table I
Parameters used for Nucleation Fits

SiO₂ Concentration	49.4%	50.0%	50.6%	52.0%	53.0%
T_m (K)	1558.9	1563	1568.1	1570.9	1573.9
ΔS (J/mole)	56.386	56.238	56.055	55.955	55.849
σ_o (Jm ⁻²)*	0.07707	0.08891	0.07376	0.06415	0.07232
σ_T (Jm ⁻² K ⁻¹) (x 10 ⁵)*	5.38258	4.15444	6.12572	7.459245	6.73961
B (K)**	1680.27	1680.27	1680.27	1680.27	1680.27
T_o (K)**	737.44	737.44	737.44	737.44	737.44
D_o (m ⁻² s ⁻¹ K ⁻¹) (x 10 ²¹)**	1.732	1.521	1.370	0.876	0.776
T_{peak} (K)***	865	867	863	860	861

*Interfacial free energy - $\sigma = \sigma_o + \sigma_T T$

**Diffusion coefficient - $D = D_o T \exp \left(- \frac{B}{T - T_o} \right)$

***Calculated Peak Nucleation Temperatures